

The Lower it Goes, The Tougher it Gets!

The Practical Implications of Producing Ultra-Low Sulfur Diesel (ULSD)



Our Technology Touches the World

UOP 4080C-1

***Sulfur, How &
How Low?***

***Cetane?
Aromatics?
Distillation?***

***What About
Fuel Oil?***

***Grade
Segregation?***

***Fuel Cells?
Hybrids?***

***Off-Road
Diesel Specs?***

***Alternative
Diesel Fuels?***

The Lower It Goes, The Tougher It Gets!



- What is ULSD and why is it so difficult to produce?
- Can you revamp your existing unit?
- What are the operational and refinery issues?
- What are the capacity and flexibility issues?

What Is Ultra-Low Sulfur Diesel?



Will Diesel Engines Power
Tomorrow's SUVs?

- 500 wppm S has been a common world specification.
- The EU spec will be likely be 10 ppm at the refinery gate
- The Swedish class one limit is 10 ppm S
- In the US, most refiners are designing for 5 to 8 ppm out of their hydrotreaters

Hydroprocessing Solutions to Clean Fuels

- **ULSD Fundamentals: Feed issues**
- **Revamp issues**
- **New unit design considerations**
- **Other issues**



Sulfur Species Reactivity

Sulfur Species

Thiophenes

Benzothiophenes

Non-Thiophenes

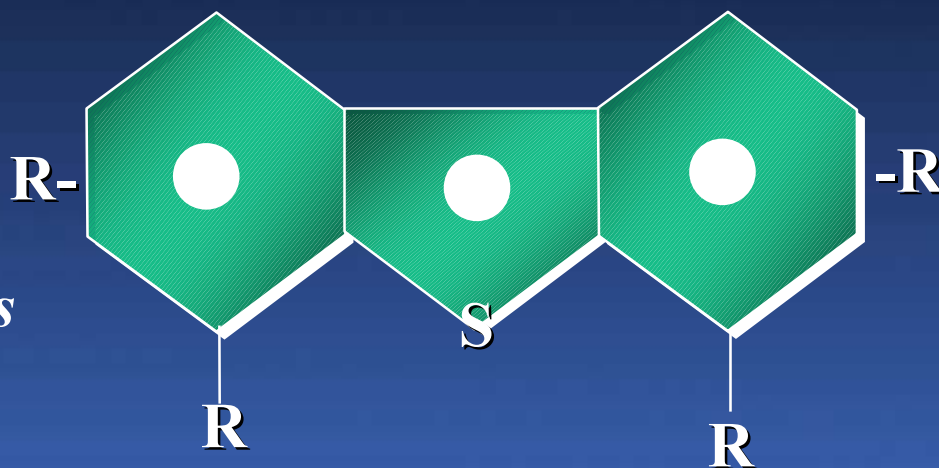
Dibenzothiophenes

Mono-Beta-Dibenzothiophenes

Di-Beta-Dibenzothiophenes

Reactivity

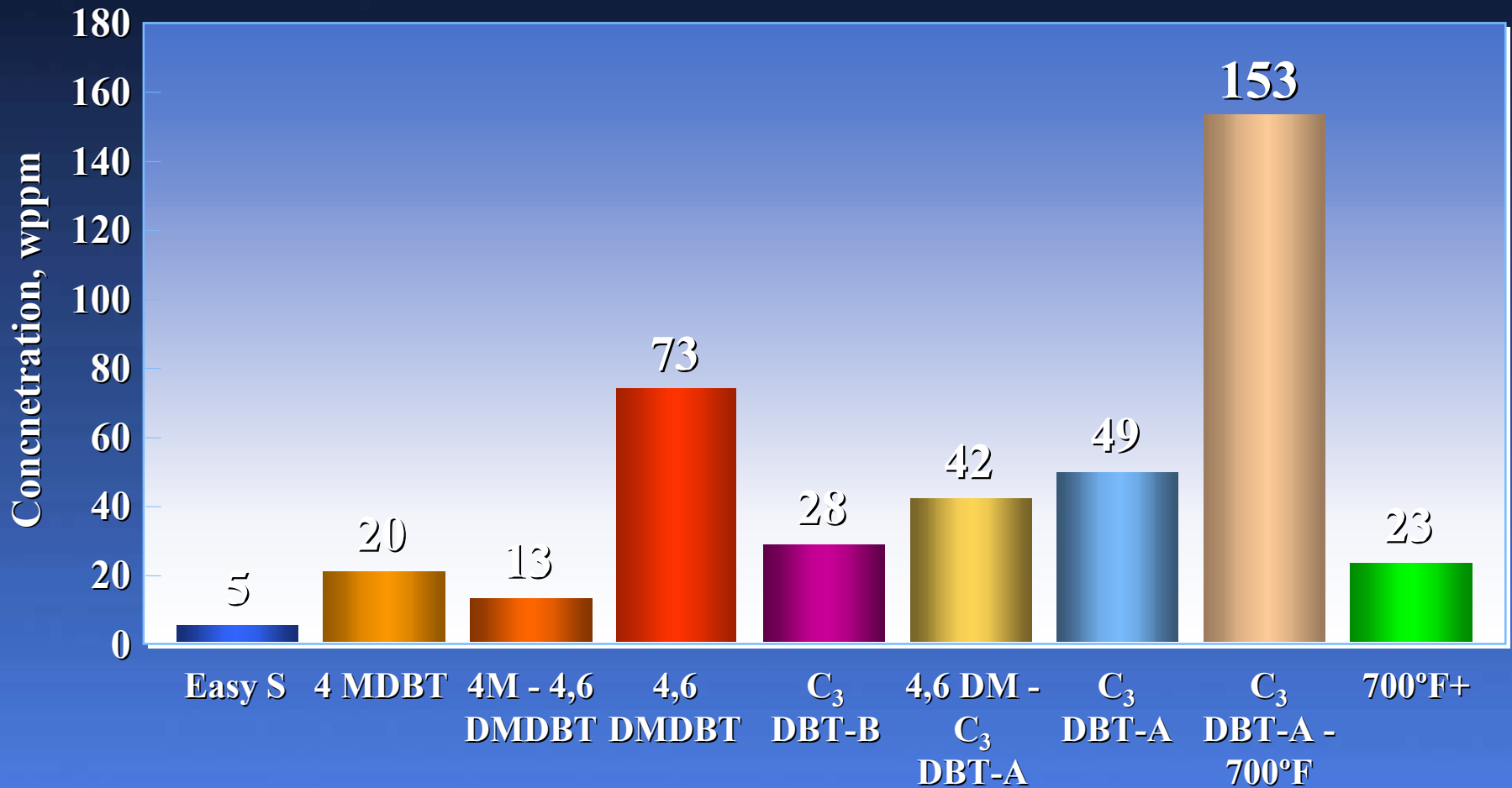
Most Difficult Species



Beta substituted-Dibenzothiophene Family

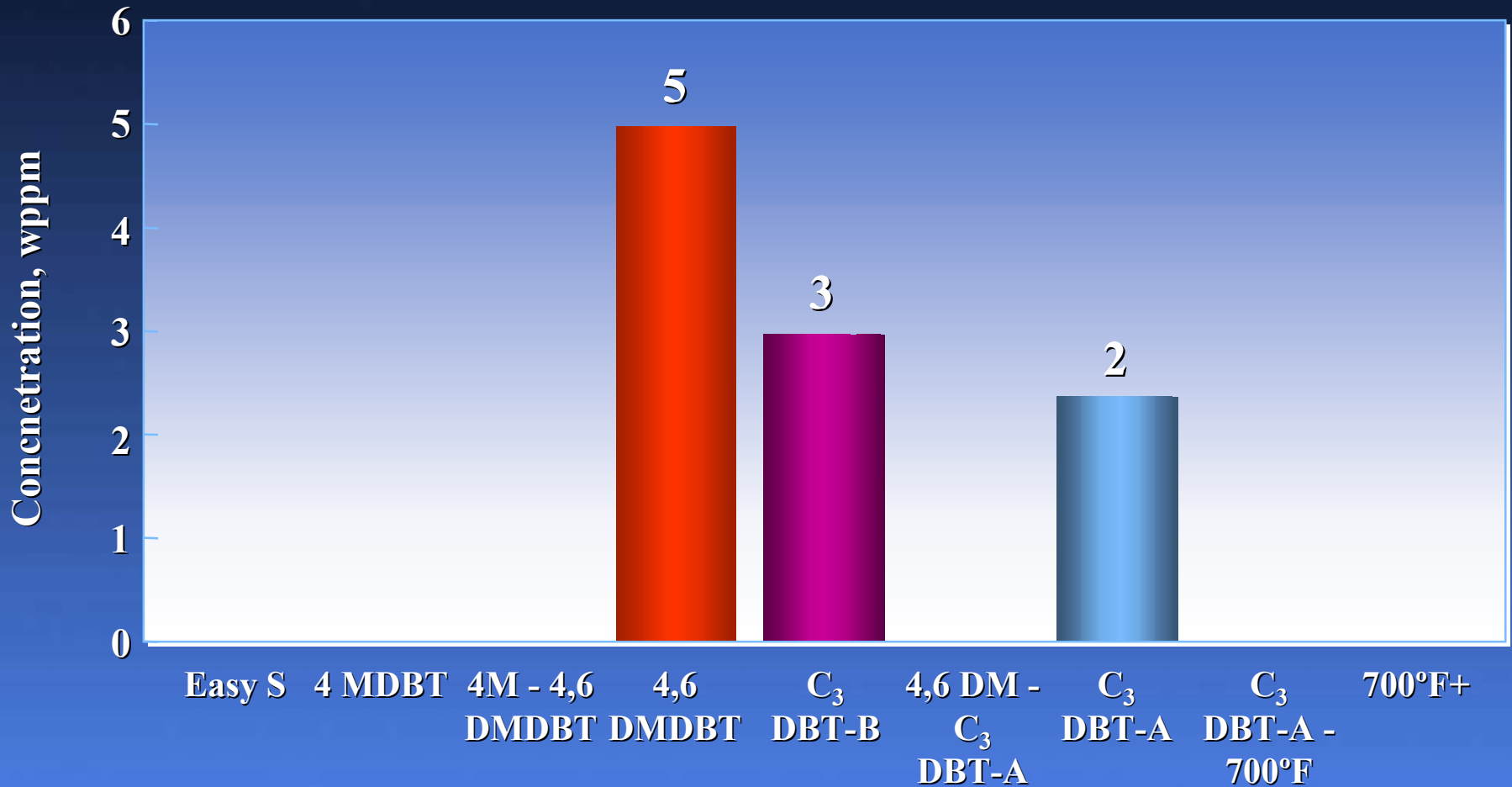
Concentration of Sulfur Species

Total Sulfur = 405 wppm

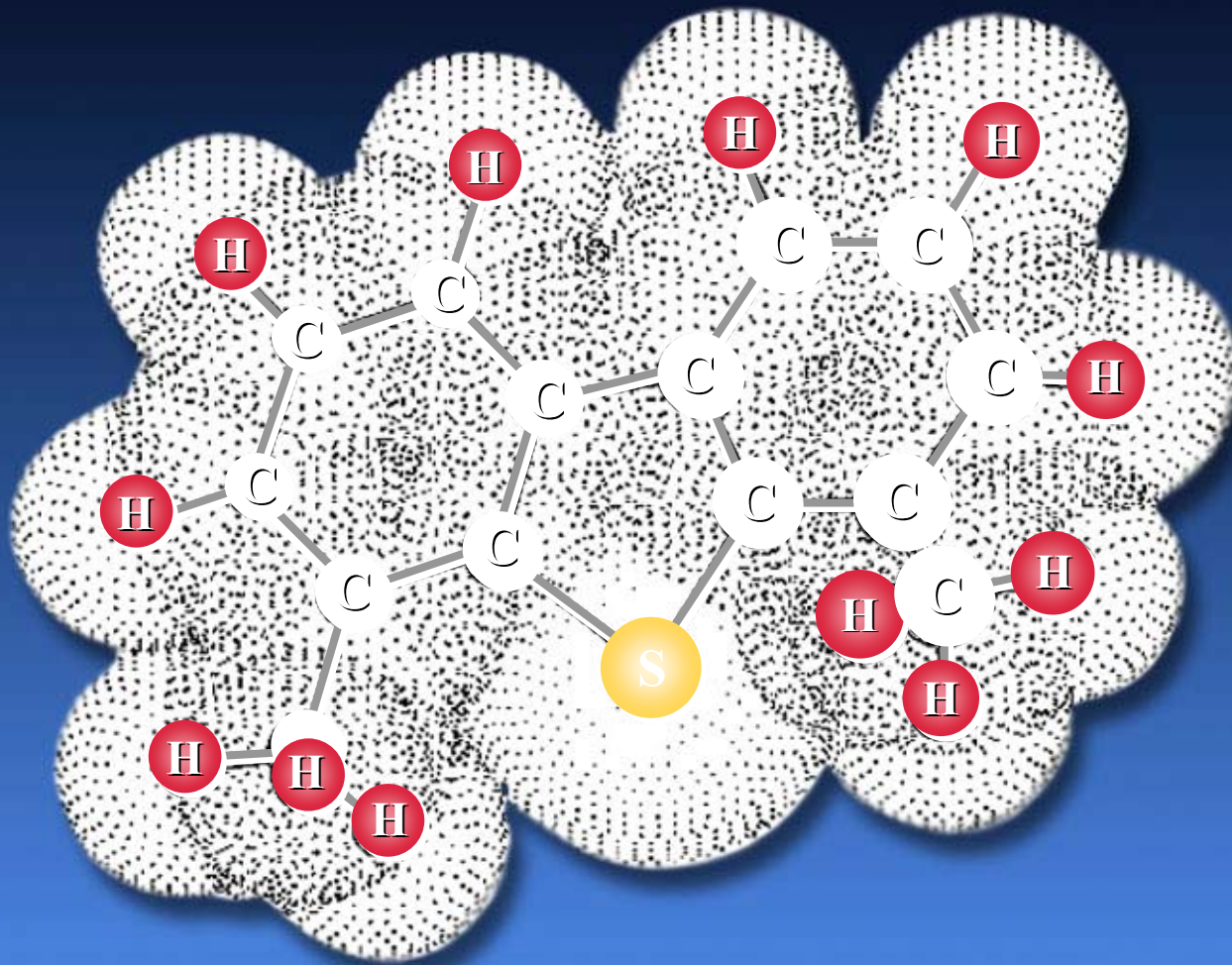


Concentration of Sulfur Species

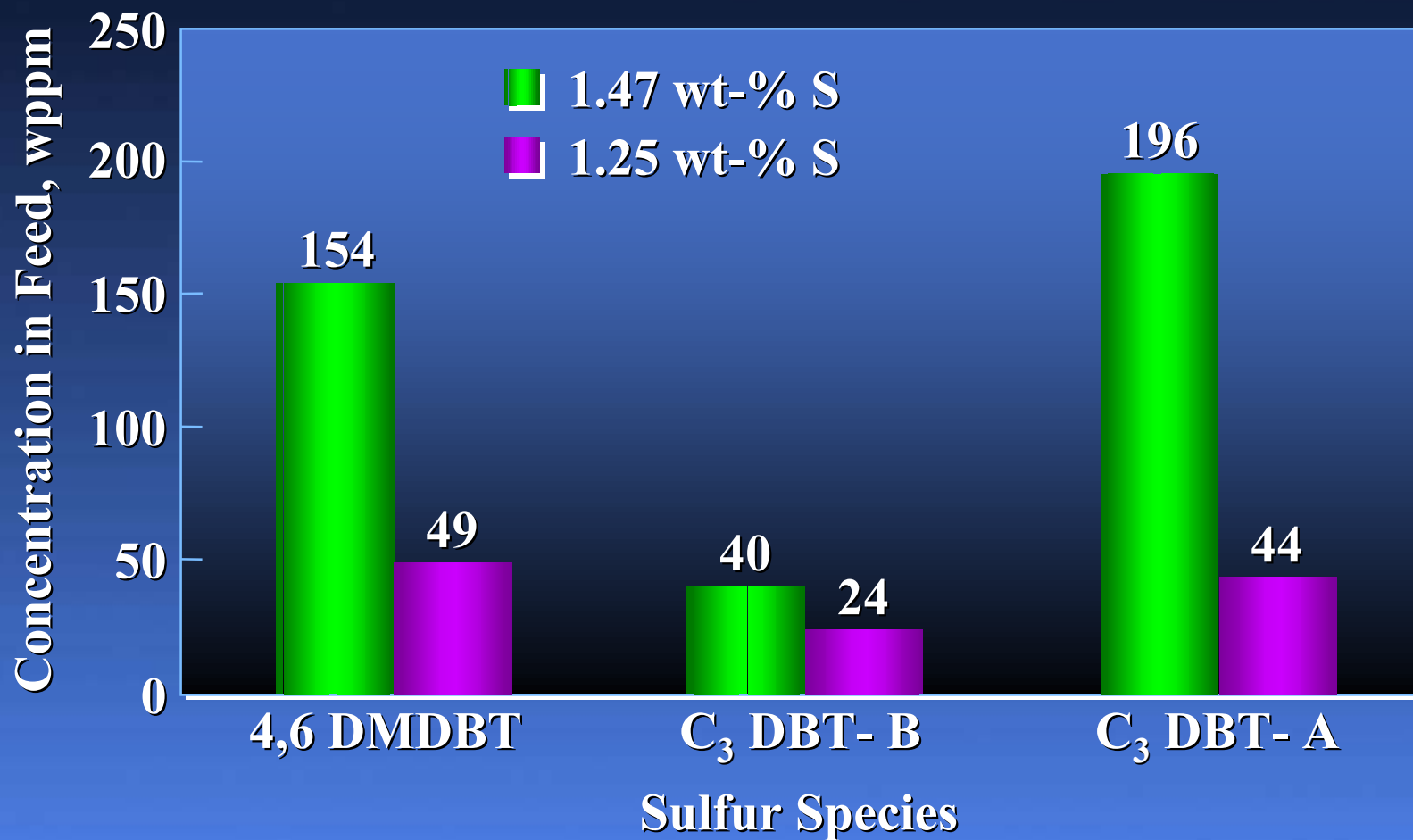
Total Sulfur = 10 wppm



4,6-Dimethyl-Dibenzothiophene

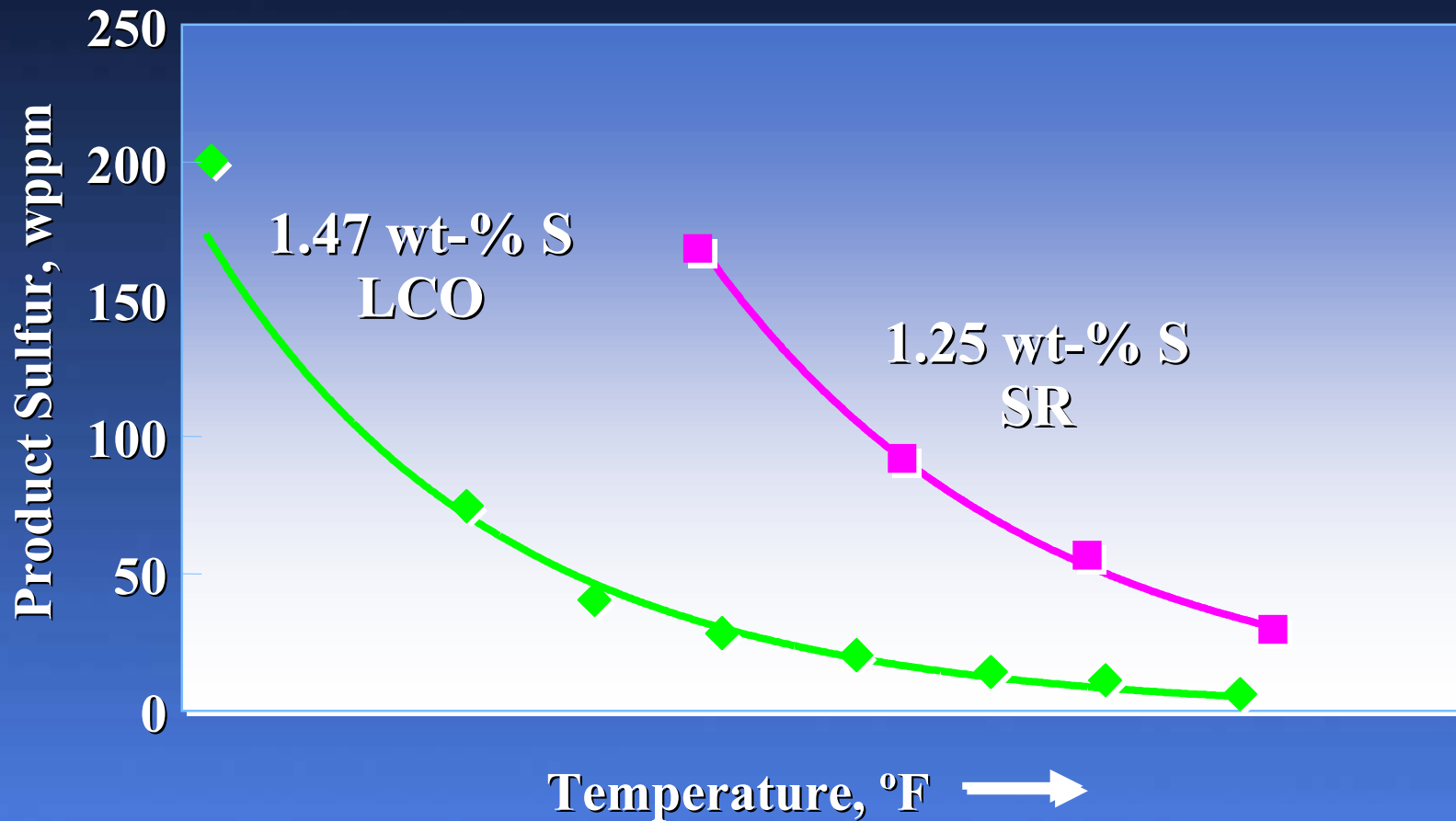


Concentration of Sulfur Species in Two Feedstocks



Product Sulfur vs. Temperature

Catalyst = Ni/Mo P = 600 psig (LCO) P = 500 psig (SR)



ULSD Fundamentals

Feed Issues

- Feed Total Sulfur Content is *not* a predictor of process severity required to achieve ULSD product
- Knowledge of the concentration of three
 - 4,6 Dimethyl dibenzothiophene
 - C₃ DBT-B
 - C₃ DBT-Ais *essential* in determining the process conditions required to achieve ULSD

ULSD Fundamentals

Feed Issues

- Feed Nitrogen Content is a *critical* parameter
- Reactivity of Nitrogen compounds *must* be considered
- Desulfurization and Denitrogenation are inter-related: *HDS and HDN can not be treated independently*

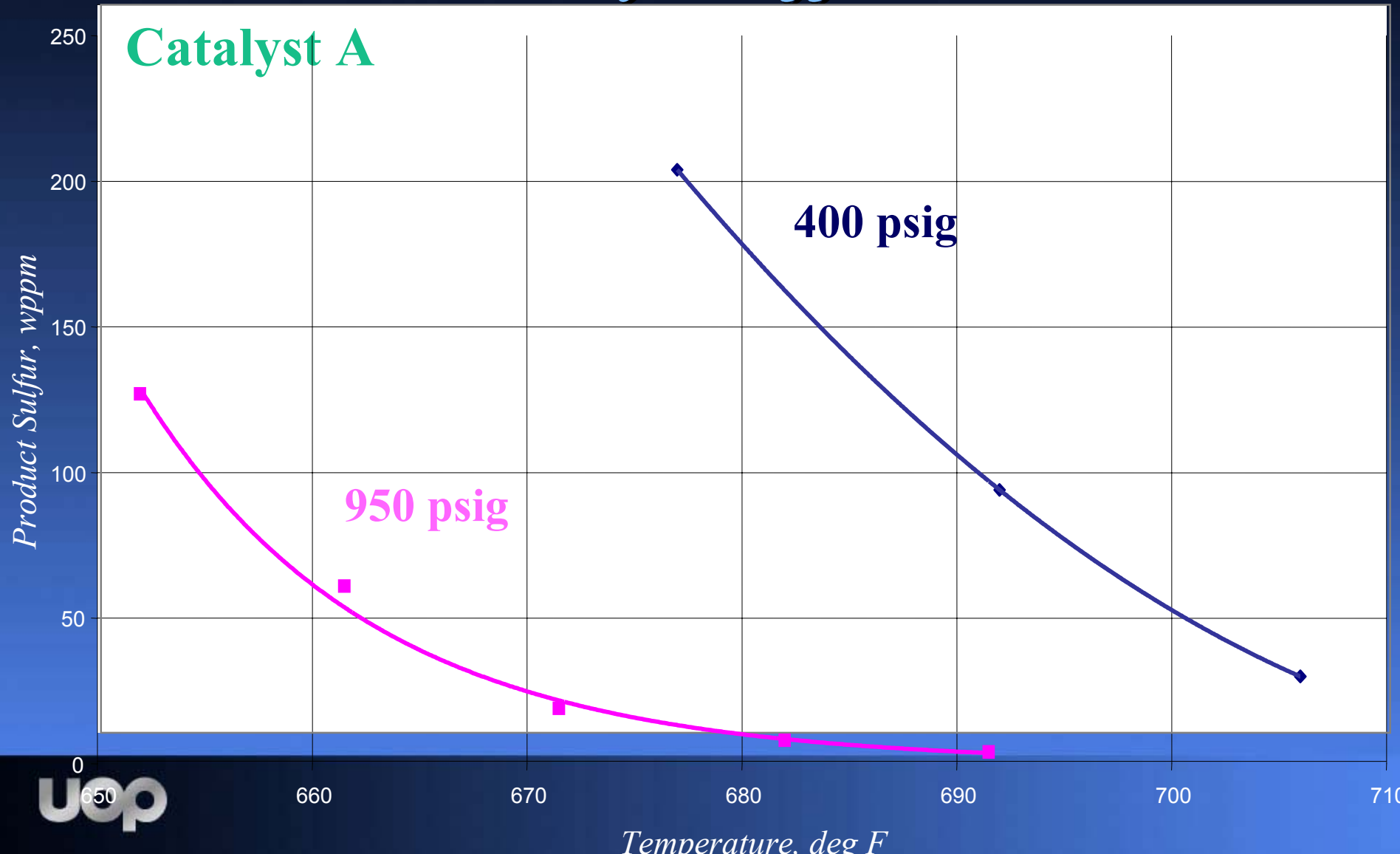
ULSD Fundamentals

More Than Just Feedstock

- **Feed Effect**
 - Sulfur
 - Nitrogen
- **Catalyst Effect**
 - What type of catalysts
 - Relative activities of commercial catalysts

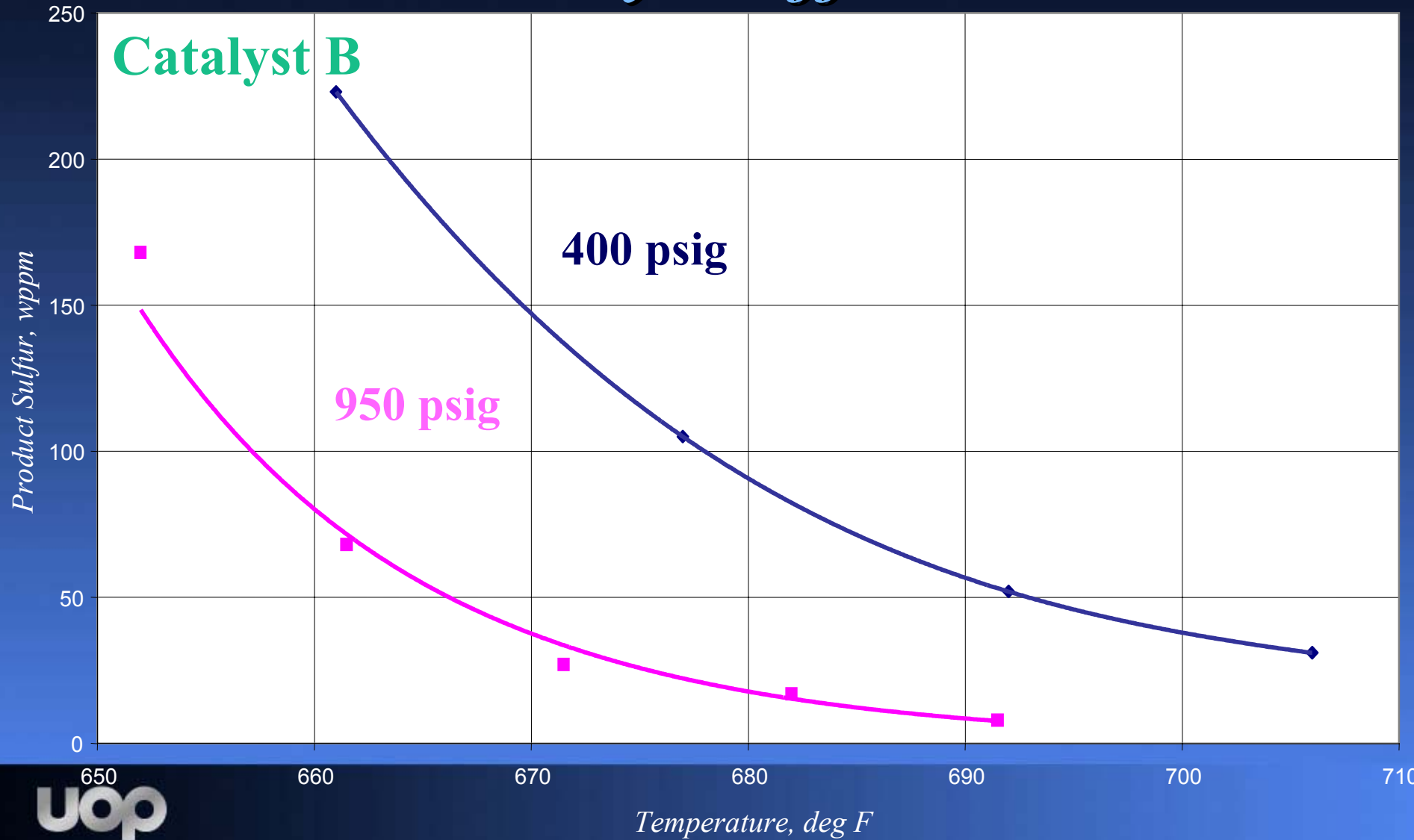
ULSD Kinetics

Catalyst Effect



ULSD Kinetics

Catalyst Effect



ULSD Fundamentals

- *At ULSD (~ 10 wppm S), all sulfur species have disappeared except for three*
- *Desulfurization and Denitrogenation are inter-related*
- *Catalyst type and activity affect the performance*
- *Hydrotreating unit operating conditions are equally important*

Hydroprocessing Solutions to Clean Fuels

- **ULSD Fundamentals: Feed issues**
- **Revamp issues**
- **New unit design considerations**
- **Other issues**



Process Objectives

Consistent Performance

- Need robust design to produce ULSD day in and day out

Reliability is Key

- At <10 ppm S, off spec. products can not be blended off & need to be re-processed

No By-passing

- A small degree of by-passing or mal-distribution in the reactor will lead to off-spec. materials

*Need best designed and well run
unit to produce ULSD*

Revamp Issues

- The “Heart” of the unit: The Reactor

Factors affecting Reactor Performance

Internals

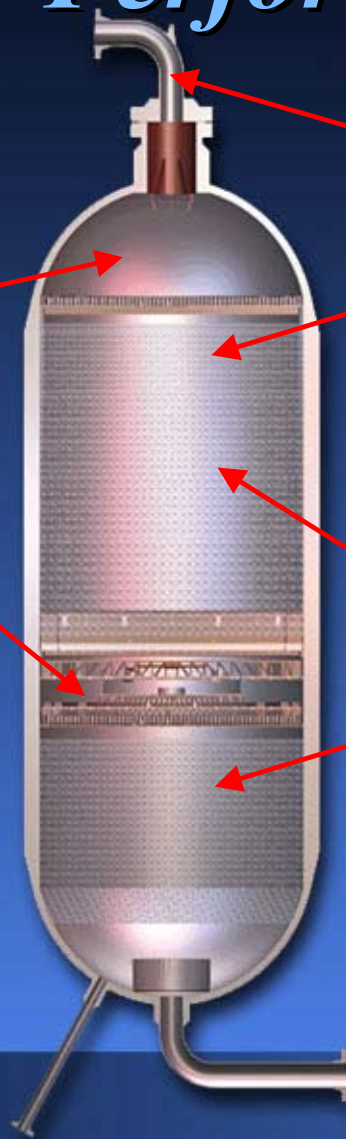
Vapor-liquid
distribution
Thermal mixing
Maintenance

Operations

Liquid and gas rates
Poor startup
Fouling
Upsets
Runaway

Loading

Sock vs. dense
Catalyst handling
Loading profile



Revamp Issues

- The “Heart” of the unit: The Reactor
- The Rest of the unit

REVAMP ISSUES

Fresh
Feed

Gas/Oil ratio ?

Refinery
H₂ Balance?

New
Rx

Rx

PSA

Make-up
H₂ Purity?

 = New
Equipment

H₂S
Scrubber?

HPS

Stripper

*8-10 ppm S
Diesel*

Cycle Length?

Other Considerations in Making ULSD

- Cetane
- Density
- Flash
- Cold flow
- Lubricity
- Color
- Viscosity

Hydroprocessing Solutions to Clean Fuels

- ULSD Fundamentals: Feed issues
- Revamp issues
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- Other issues



Technology Options for Hydroprocessing Units

LP	HP	VGO HTU	MHC	HC	HC
U	U	+	+	+	
L	L	U	U	U	
S	S	L	L	L	
D	D	S	S	S	
		D	D	D	



Compliance
No ROI

Compliance
Potential
ROI

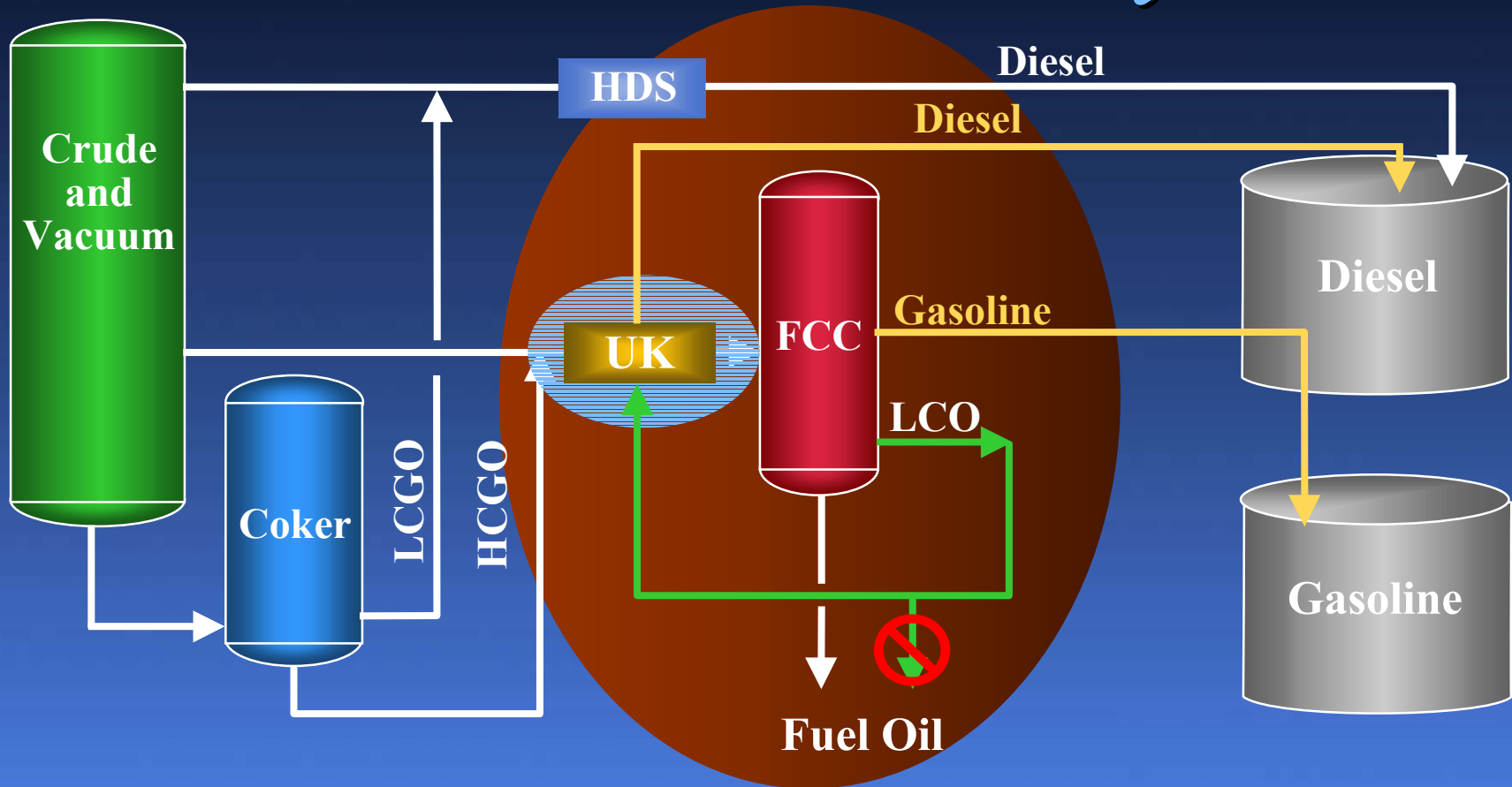
Compliance
Potential
ROI
Flexibility

Compliance
Good ROI
Flexibility

One Example

Partial Conversion Unicracking

Increases Flexibility



What Are the Implications?

**Operating
Issues?**

**Revamp
or New Unit?**



A New Set of Operating Issues



- Is it reliable enough?
- You can't run at 5 wppm S
 - Feed changes
 - Compliance margins
- Feed bypassing
 - Reactor maldistribution
 - Leaking heat exchangers

What Are the Implications?

**Operating
Issues?**

**Revamp
or New Unit?**

**Refinery
Issues?**

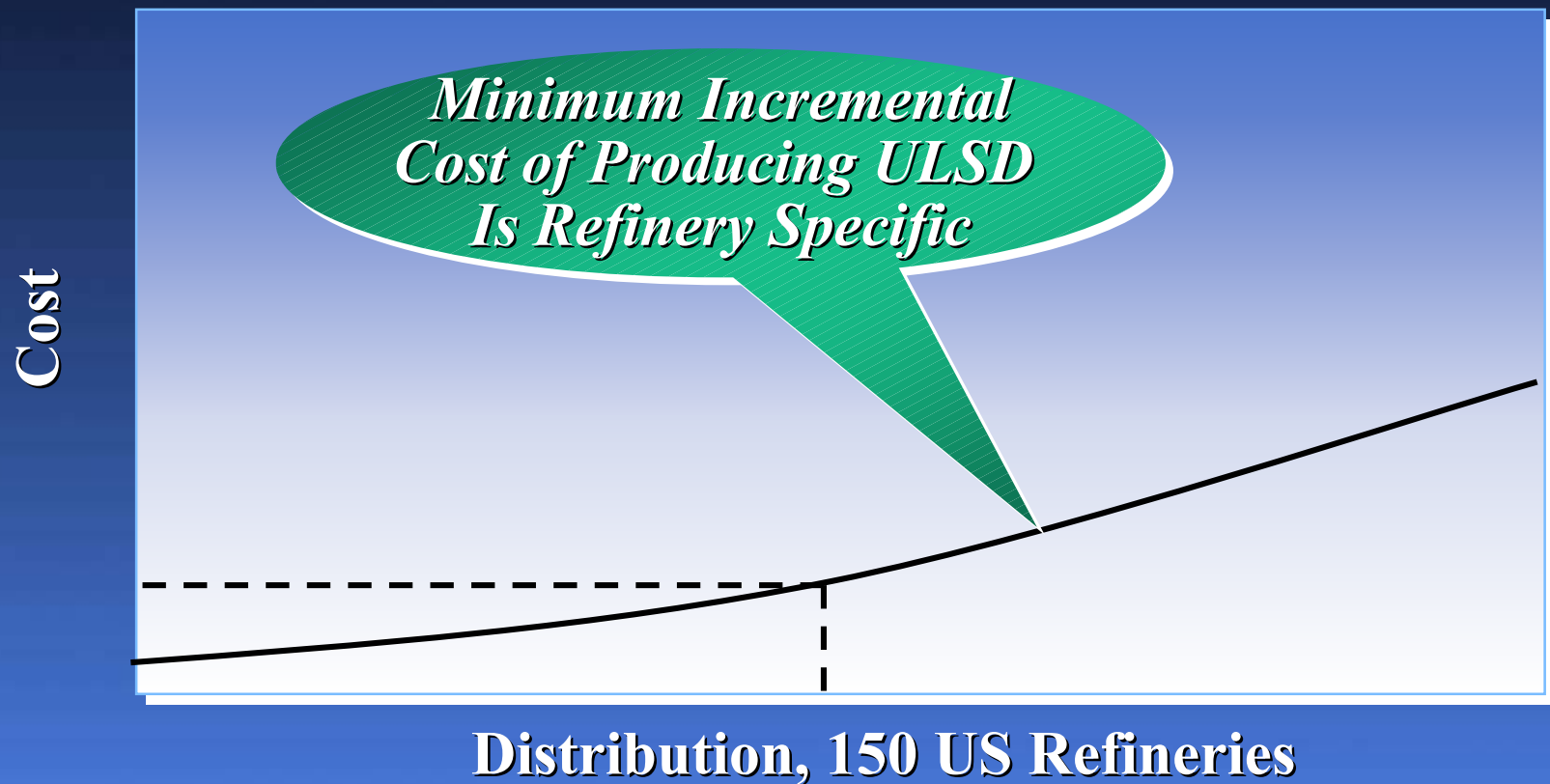


Refinery Implications



- Requirements for system cleanup
- Product segregation costs
 - Manifolding
 - Proof tanks
- Increased hydrogen demand
- Product distribution

Median Cost of Producing ULSD



What Are the Implications?

**Operating
Issues?**

**Revamp
or New Unit?**

**Refinery
Issues?**

**Diesel
Volume?**

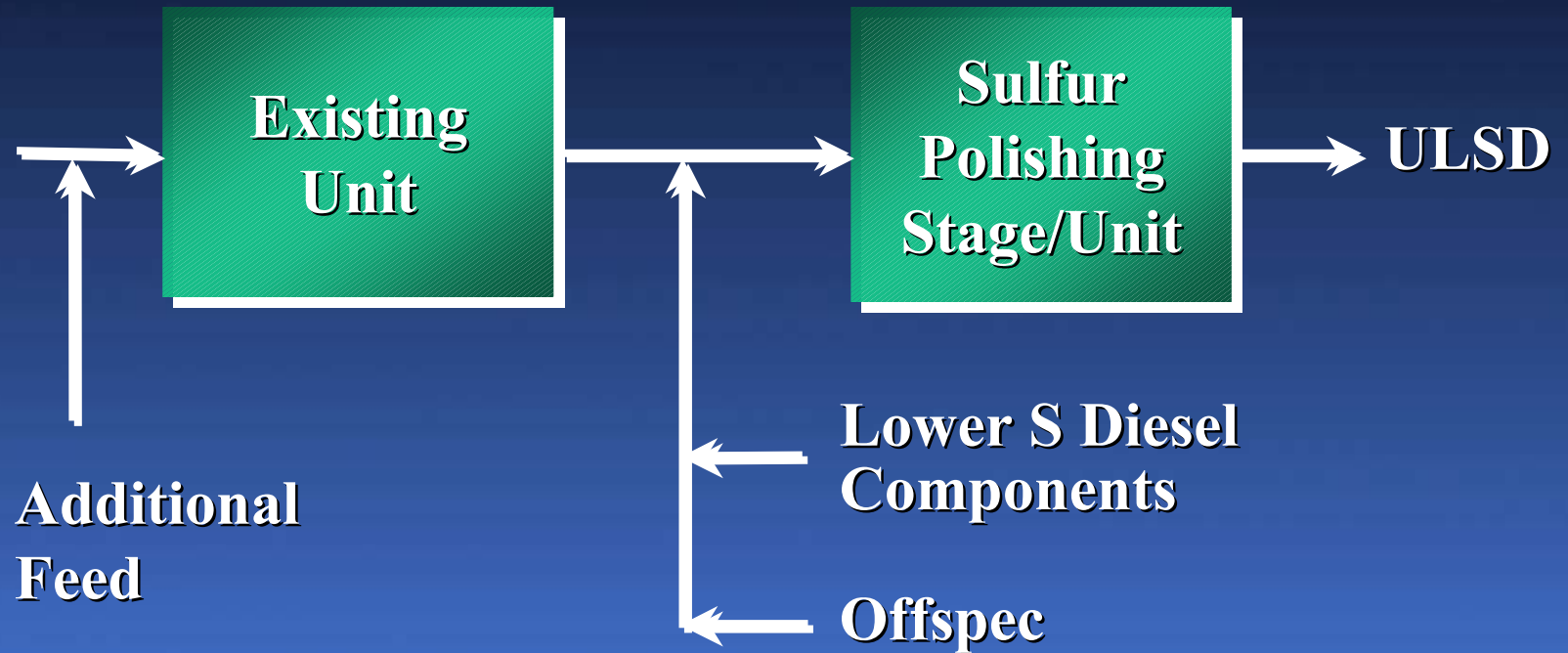


Capacity Implications of ULSD

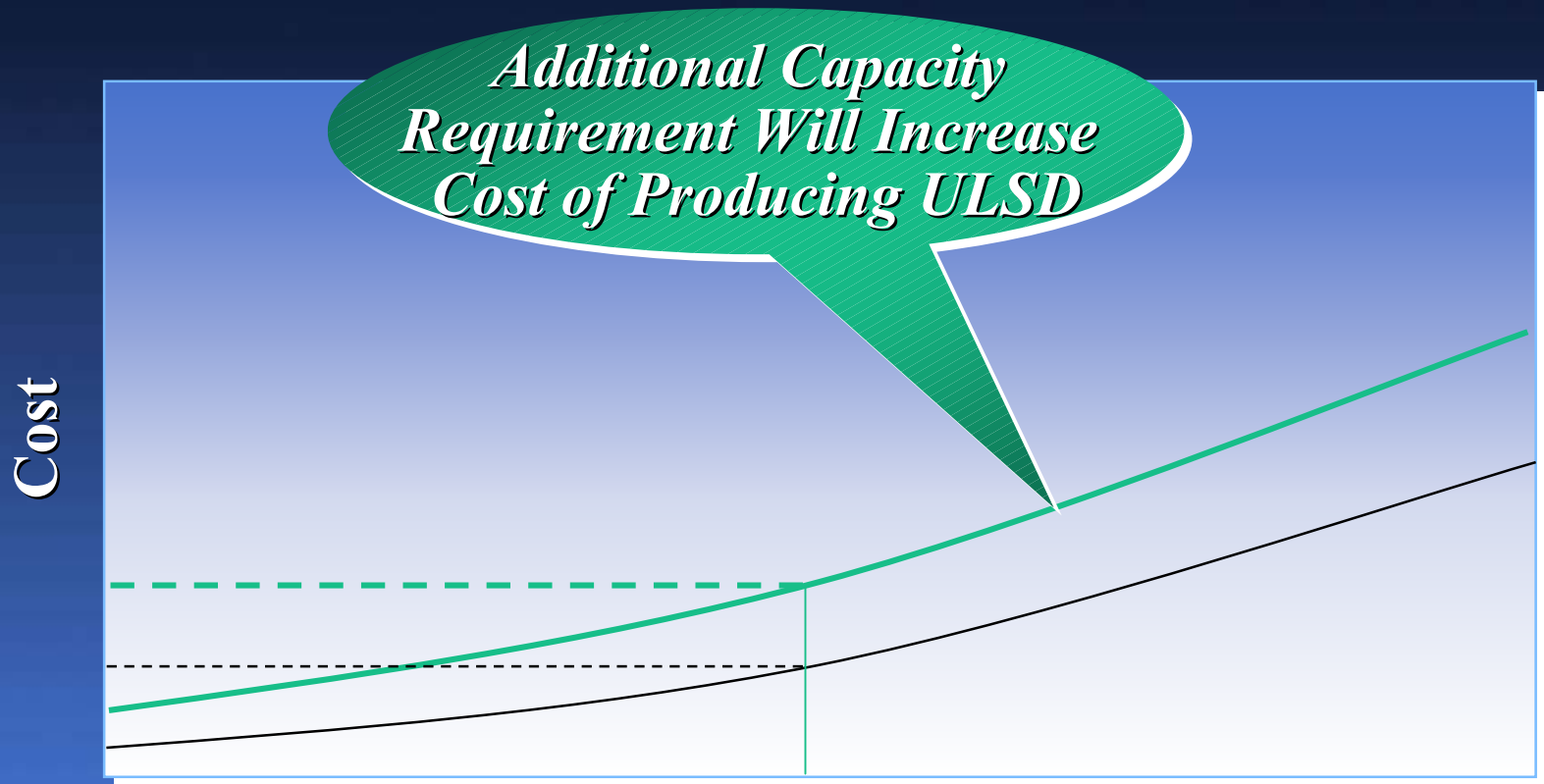


- **Yield loss**
- **Must process materials that were previously high quality blend stocks**
 - Hydrocracked diesel
 - Merox treated kerosene
- **Reprocessing flexibility**
 - Startup, shutdown and emergency procedures
 - Routing of offspec material

Capacity Implications of ULSD



Median Cost of Producing ULSD



Distribution, 150 US Refineries

What Are the Implications?

**Operating
Issues?**

**Revamp
or New Unit?**

**Refinery
Issues?**

**Diesel
Volume?**

Flexibility?



Flexibility for the Future

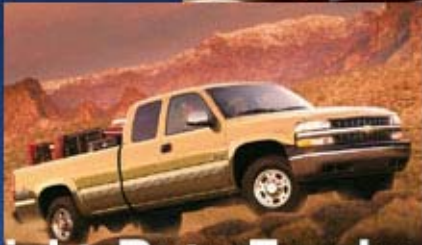
Bus Fleets



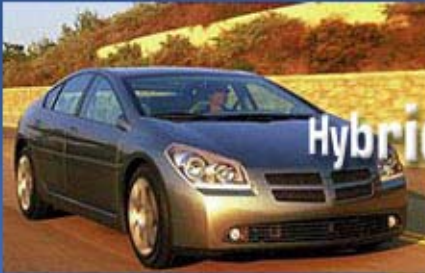
Heavy Duty Trucks



Light Duty Trucks



Hybrid



Passenger Cars

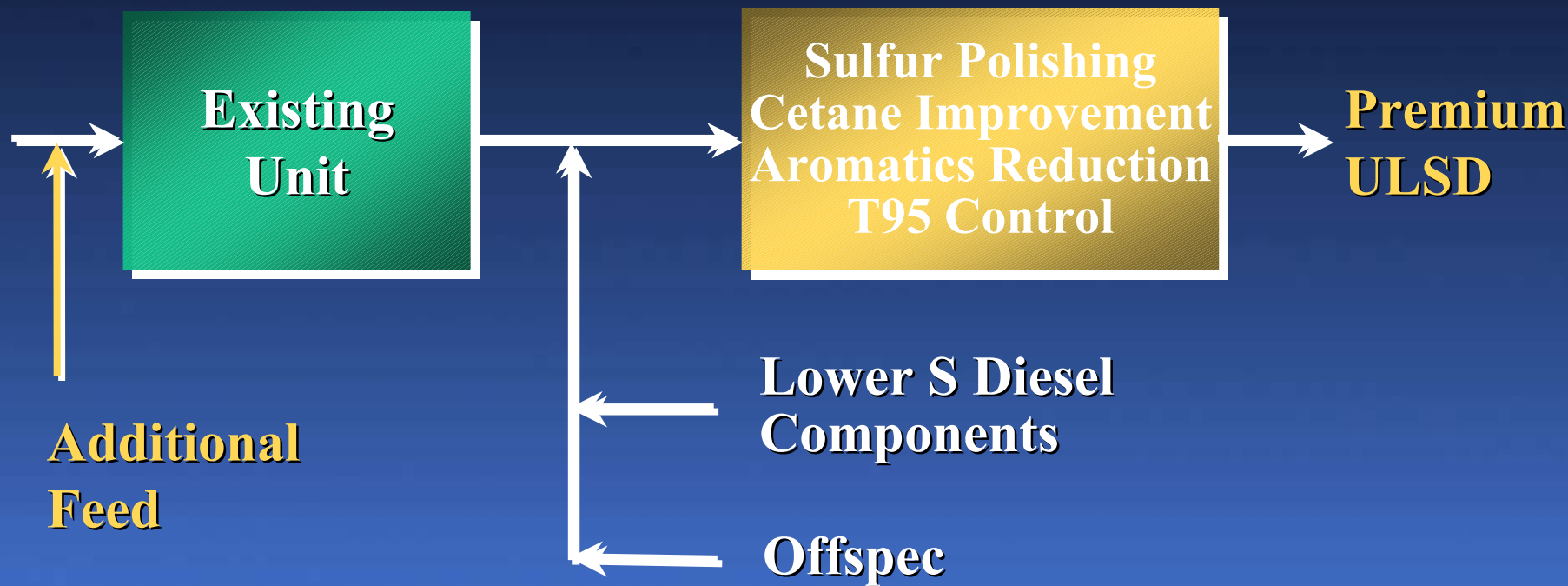


Fuel Cell

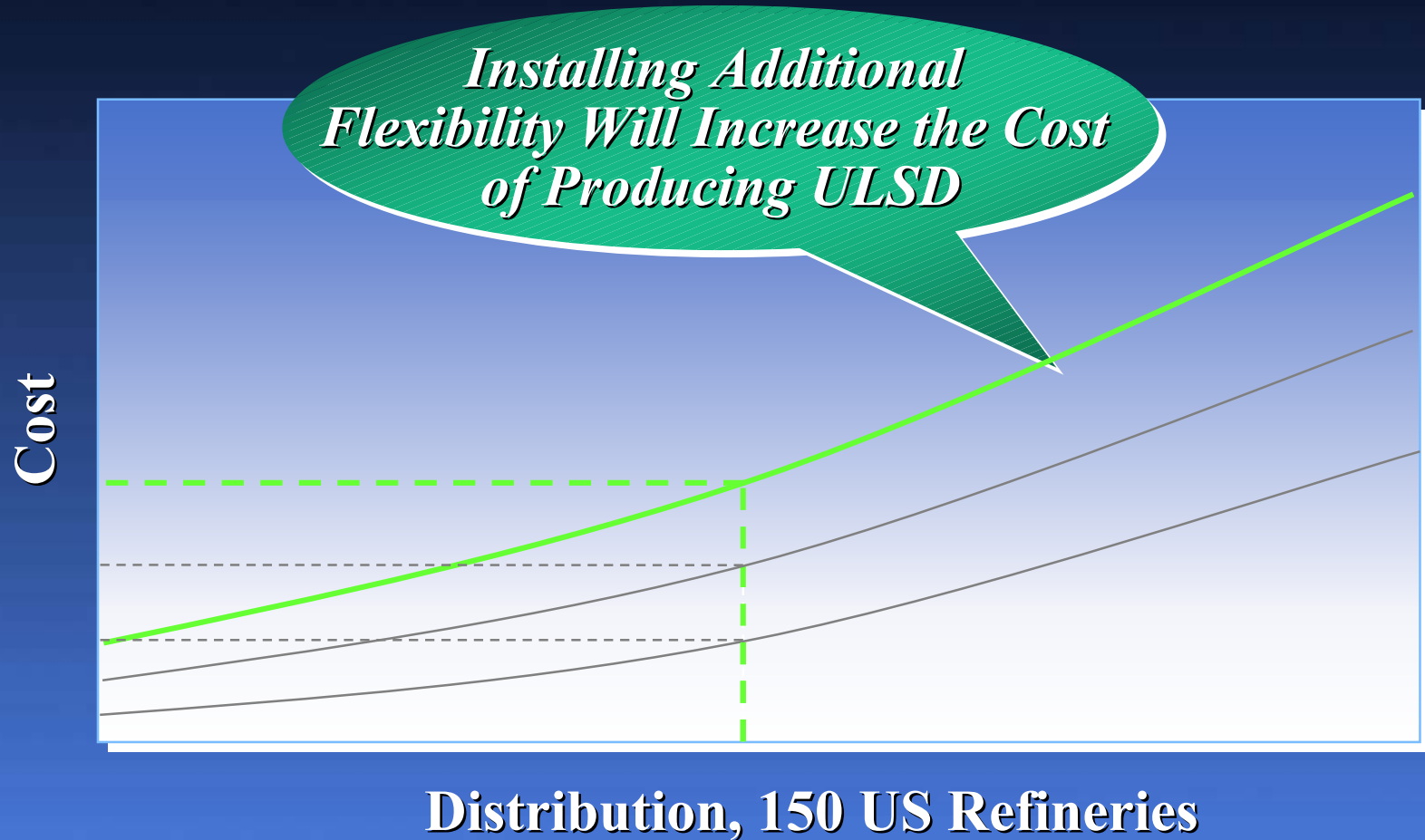


- Expansion of diesel fuel market
- Off road diesel
- Evolving diesel specifications
 - Cetane?
 - Aromatics?
 - T95 distillation?
- More difficult feeds

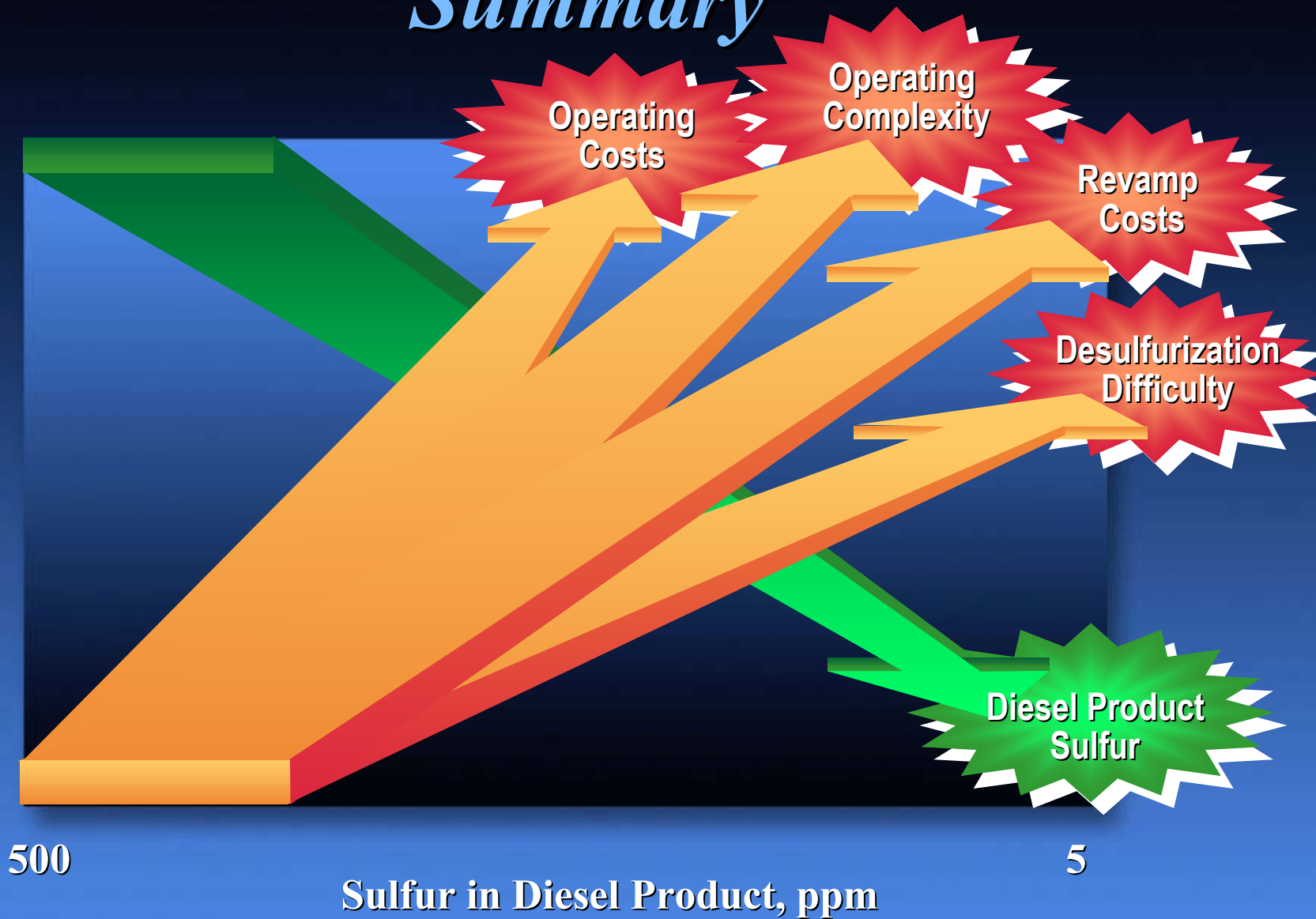
Flexibility Implications of ULSD



Median Cost of Producing ULSD



Summary



Conclusions



- Making ULSD is similar to making a high purity chemical
- Unit operations and product distribution will be more complex and more expensive
- Simple unit revamps may not be enough
- Couple short term plans for ULSD with strategies for diesel product flexibility to achieve the most cost effective, long term solution

Q & A

